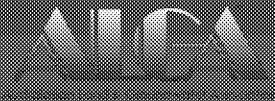


Fluorochemicals

- the New Bad Kid on the Block !!

Dr Jimmy Seow
Manager Pollution Response
Department of Environment Regulation WA
Adjunct Associate Professor Curtin University WA
Email: jimmy.seow@der.wa.gov.au

ALGA Talk
Canberra and Brisbane
22 – 23 April 2015



Government of Western Australia
Department of Environment Regulation

Profile

- More than 30 years working experience in environment, health and safety, emergency response, policy, oil gas, mining, technology and research
- Currently Manager Pollution Response, DER WA
- Member several state emergency management committees
- Member CRC Care Technical Working Group on PFC
- Adjunct Assoc Professor Curtin University WA
- PhD in soil science and catchment hydrology UWA

How Are You All Affected – 7 Habits of Fluorochemicals (FC)

1. FC is a pollutant – Pollution Response, fire fighting waste water with FC
2. FC contaminated sites
3. FC transport – Controlled Waste Regulation M160 in Schedule
4. Landfill disposal – Landfill license acceptance conditions for FC
5. FC treatment by incineration – license conditions
6. Premises licensing – premises that use foam with FC
7. Policy – regulatory and organisation position on use of foam with FC

Format of the talk

1. Overview on the environmental and human health concerns of fluorochemicals
2. Overview on fluorochemical terminology and chemistry
3. Fluorotelomers
4. Short versus long chain fluorochemicals
5. Current legislative and policy thinking and direction in Australia and overseas

Summary - 1

- More and more fluorochemicals found in the environment coming from:
 - Direct – industrial, commercial and consumer uses
 - Indirect – precursors degradation to PFOS PFOA
- Goes ultimately into surface and groundwater then the ocean
- Long half-lives in the environment (PFOS 41 years and PFOA 92 years in water) and humans (~ PFOS 4-5 yr PFOA 3-4 yr).
- Main concerns currently PFOS PFOA and long chain PFC.

Summary - 2

- PFOS PFOA confirmed to have PBT and CMR concerns.
- Not just PFOA but also PFNA, PFPA, PFBS, PFBA concerns.
- Fluorotelomers health impact not sure yet although 6:2 FTS seem to be less toxic and bioaccumulative than PFOS but still persistent.
- PFOS now banned and PFOA now in process of being phased out or already ban.

Summary - 3

- New fire fighting foams should no longer have PFOS PFOA but rogue countries do it.
- New forms use short chain C6 fluorotelomers (6:2 FTS) but can have PFOA purity issue.
- Long chain fluorotelomers such 8:2 FTS, 10:2 FTS and longer are of concerns as it can degrade to PFOA.
- Fluorine-free fire fighting foams are now commercially available on the market and many using it but is NOT the Holy Grail.

Summary - 4

- Regulatory agencies tightening up their regulation and policy on the use of fluorochemicals.
- Policies emerging for stricter control on the use of foams with fluorochemicals during operation and training.
- Legacy issue – remaining old stocks of foams with PFOS PFOA.
- No screening values for soil, sediment, surface water and groundwater contaminated with PFOS, PFOA and certainly none for fluorotelomers
- MDCH new guidelines for fish consumption for PFOS

Summary – 5

- Range of different drinking water and soil screening values. None for Australia – interim Qld foam policy ? And CRC Care Project
- Currently treatment for fluorochemicals in soil or fluorochemicals itself is by thermal incineration at high temperature > 900 C to break the C-F bond – expensive or thermal desorption technique in conjunction with other removal techniques for the released F.
- Water contaminated with fluorochemicals via methods of absorption and filtration or its combination – can be expensive due to volumes involved and depending on regulatory end point criteria. Many still proof of concept or pilot schemes.

Summary – 6

- New improved methods to analyse perfluorochemicals for its detail composition e.g. FAB-MS, QTOF-MS, Fourier transform cyclotron ion resonance – MS
- Regulatory issues
 - Screening values – when ? Interim Qld foam policy ?
 - Treatment license conditions
 - Landfill and disposal acceptance criteria and licences
 - Premises licence to use foam
 - Transport of materials with PFC

What are Fluorochemicals

- A general, nonspecific term - has carbon chains with fluorine – fully or partial fluorination (ie fluorinated)
 - Perfluorinated e.g. PFOS, PFOA
 - Polyfluorinated e.g. fluorotelomers
 - Fluoropolymers e.g. TEFLON
 - Side-chain fluorinated polymers
 - Perfluoropolyethers

Setting the scene – Uses

- Fluorochemicals widely used in many industries besides fire fighting foam due its:
 - dirt, grease and water resistance properties
 - low friction and surfactant properties
 - dielectrical properties
 - thermal stability, versatility, strength, resilience and durability

Setting the scene - Chemistry

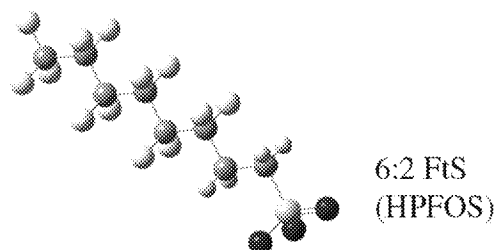
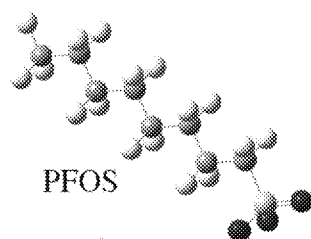
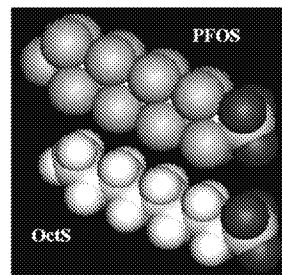
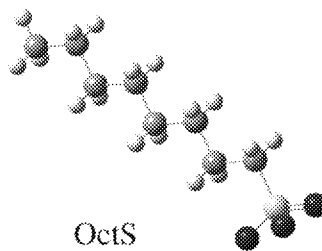
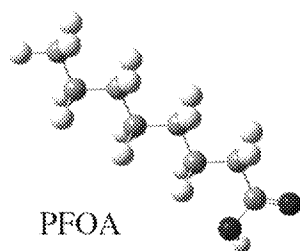
- Many synonyms, acronyms and terminology e.g.
 - PFC – Pefluorochemicals, Perfluorinated compounds
 - PFAS - perfluoroalkyl sulphonate or perfluoroalkyl sulfonic acids (PFSAs)
 - PFAC - perfluoroalkyl carboxylates or perfluoroalkyl carboxylic acids PFCA
 - perfluoroalkyl carboxylates and perfluoroalkyl sulphonates

Short Chain versus Long Chain Fluorochemicals

- Some confusion depending on who you talk to
- OECD/UNEP (2013) definition:
- “long-chain PFASs” refers to:
 - (i) PFCAs with 7 and more perfluoroalkyl carbons, such as PFOA (with 8 carbons or C8 PFCA) and PFNA (with 9 carbons or C9 PFCA);
 - (ii) PFSA s with 6 and more perfluoroalkyl carbons, such as PFHxS (with 6 perfluoroalkyl carbons, or C6 PFSA) and PFOS (with 8 perfluoroalkyl carbons or C8 PFSA); and
 - (iii) Substances that have the potential to degrade to long-chain PFCAs or PFSAs, i.e. precursors such as PASF- and fluorotelomer-based compounds.
- Buck et al 2011 published a paper to sort it all out.

Setting the scene – Policy/regulation

- Emerging issues for regulators world wide
- No detail policy on the use of fire fighting foams
- No screening values for contaminated sites other than drinking water guidelines
- Fluorine free foam versus foam with fluorotelomers.
- Regulatory terms - ban, restrict, listing, submissions, proposals



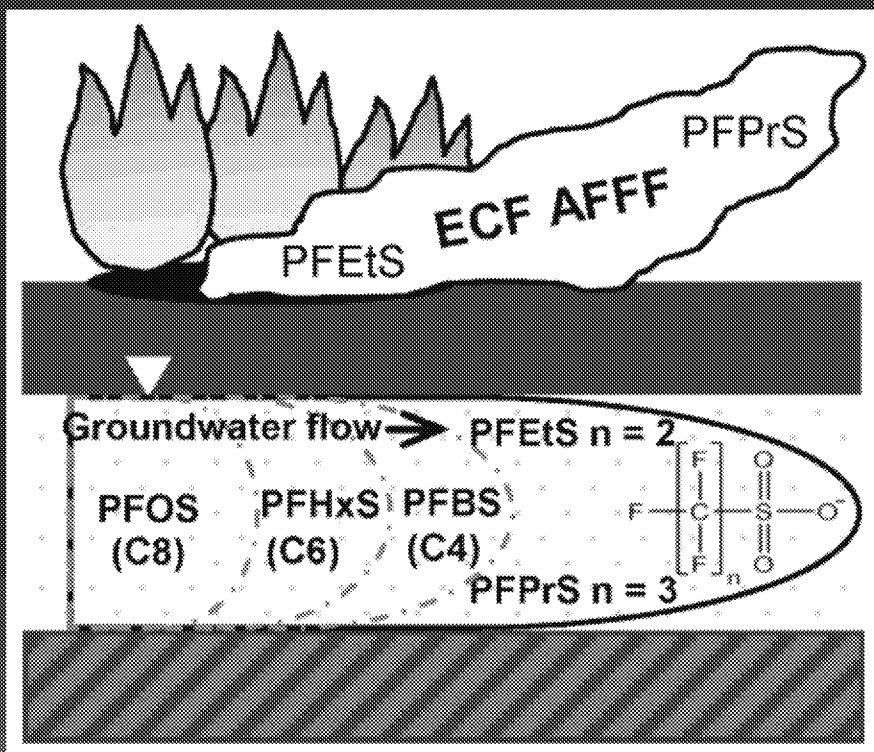
Dark grey – carbon
Light blue – fluorine
Red – oxygen
Small grey – hydrogen
S - sulphur

R.A. Klein, Australia 2009

Legacy AFFF issue




Aurora*
environmental



Adapted from Barzen-Hanson and Field, 2015

Fluorotelomers

- Produce by telomerisation process and NOT electrochemical fluorination
- Fluorotelomers consist of a perfluorinated (i.e. perfluoroalkyl) moiety, usually C6 or C8
- Fluorotelomers technically not perfluorinated but still persistent – still a cat ! Still a perfluoroalkyl substance !
- All modern AFFF agents contain telomer-based fluorosurfactants and do not contain or break down into PFOS or its homologues such as PFHxS (perfluorohexane sulfonate)
 - its long chain fluorotelomers and precursors such 8:2 FTS and 10:2 FTS degrades to PFOA
 - C6 fluorotelomers degrades to 6:2 FTS and PFHxA
- Like PFOS and PFOA also pervasive in the environment
- Telomer-based foams are not banned or restricted from use
- Foam manufacturers are in the process of transitioning to the use of pure C6-based fluorosurfactants



**What are
regulators doing
about it ?**

1980	UK	EU Groundwater Directive to prevent the discharge of organohalogen compounds and substances into the aquatic environment..."
2000	3M	3m discontinued making PFOS
2002	USEPA	Initiated voluntary phase out of PFOS
2004	UN	Stockholm Convention on POPs Australia ratified and became a party
2005	Sweden	Sweden <u>PROPOSED</u> to add PFOS to Stockholm Convention Annex A
2005	EC	Directive to <u>RESTRICT</u> the use of PFOS in carpets, textiles, clothing and other items
2006	EU	EU Directive to <u>RESTRICT</u> the marketing and use of PFOS-based foams and 27 June 2011

2006	UK	UK Environment Agency policy on the disposal of firewater containing PFOS
2006	USEPA	2010/15 PFOA Stewardship Program to reduce and eliminate facility emissions and product content for PFOA and PFOA related chemicals by 95 % by 2010, and to phase out PFOA and PFOA related chemicals including potential PFOA precursors by the end of 2015
2007	UK	UK Environmental Agency policy on disposal of liquid effluent containing PFOS
2007	Norway	<u>BAN</u> PFOS in fire fighting foam and proposed to ban PFOA in products
2008	Canada	Environment Canada <u>REGULATED</u> and <u>PROHIBITED</u> the manufacture, use, sales and offer for sale and import of PFOS into Canada

2008	EU	EU Regulation prohibited use of PFOS in fire fighting foam and ban on textiles and impregnating agents containing PFOS
2008	Dupont	Reduce PFOA content in aqueous based dispersion from range of 1000 ppm to 5000 pm to below 50 ppm
2009	USEPA	Long-Chain Perfluorinated Chemicals (LC-PFCs) Action Plan to <u>BAN</u> or <u>RESTRICT</u> the manufacture, processing and use of those chemicals
2009	Canada	<u>PROHIBITED</u> the manufacture, import, use and sale of PFOS, its salts and precursors were under Canadian Environmental Protection Act, 1999
2009	UN	Stockholm Convention rectified to <u>BAN</u> PFOS production and use of PFOS and its salts; together with perfluorooctane sulphonyl fluoride (PFOSF) and restrict it under Annex B

2010	UN	PFOS to be added to Annex B (Restriction) of the Stockholm Convention. Australia has yet to rectify.
2010	Canada	Environment Canada <u>REGULATED</u> long-chain perfluorocarboxylic acids (PFCAs) under its Canadian Environmental Protection Act, 1999
27 January 2011		Exemption from the EU Directive allowed PFOS-based foams placed on the market before 27 December 2006 to be used until 27 June 2011 HAS ENDED and was adopted by UK Environmental Agency in February 2011 and set the limit at 10 mg/kg (10 ppm, 0.001 % w/w) PFOS on foam.
2011	Norway	<u>PROPOSED</u> regulation to <u>RESTRICT</u> the production, import, export or sale of consumer products that contain PFOA if they exceed certain limits.

2012	Norway	Fire-fighting foam containing PFOS or PFOS-related compounds in a concentration equal to or higher than 0.005 % by weight shall be delivered to an authorised facility for destruction
2012	USEPA	Significant New Use Rule for perfluoroalkyl sulfonate (PFAS) that have not yet commenced production or import long-chain perfluoroalkyl carboxylate (LCPFAC)
2012	Canada	Concluded that PFOA (C8), its salts and precursors ¹²¹ and long-chain (C9–C20) PFCAs, their salts and precursors have PBT properties but PFOA is not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health
2012	EU	REACH <u>ADDED</u> long-chain perfluoroalkyl carboxylic acids with 11 to 14 carbon atoms (C11–C14 PFCAs) to Candidate List of Substances of Very High Concern (SVHC).

2013	UK	UK Environmental Agency revised Fire and Rescue Manual encouraged FRSs to consider the use of fluorine free foam where they can satisfy themselves that the fire performance meets their needs.
2013	Denmark	Danish Environmental Protection Agency that concluded short carbon chain PFC of $\leq C6$ for perfluoroalkyl sulphonates and $\leq C8$ for perfluoroalkyl carboxylates although still persistent in the environment are less bioaccumulative and toxic than their long chain homologues.
2013	Canada	Use of AFFF having concentration of PFOS greater than 0.5 ppm will be <u>PROHIBITED</u> except for purposes relating to certain military operations.
2013	ECHA	PFOA is identified as a PBT substance and toxic for reproduction <u>ADDED</u> to REACH-Candidate List as SVHC

2013	Norway	<u>RESTRICTED</u> the production, import, export, or sale of consumer products containing PFOA in levels that exceed certain limit values but does not apply to food products, food packaging, fertiliser, tobacco, medicine, means of transport, permanently mounted equipment for means of transport and tires and similar accessories for means of transport.
2013	USEPA	Significant New Use Rule requiring companies to report their intent to manufacture or import products containing LC-PFCAs as intended for use as part of carpets or to treat carpets or importing carpets with LC-PFCAs.
2013	Canada	PFOA and its salts, perfluorinated alkyl group with molecular formula C_nF_{2n+1} in which $n = 7$ or 8 , Perfluorocarboxylic acids that have the molecular formula $C_nF_{2n+1}CO_2H$ in which $8 \leq n \leq 20$ and their salts (long chain PFCA) and perfluorinated alkyl group that has the molecular formula C_nF_{2n+1} in which $8 \leq n \leq 20$ as <u>TOXIC</u>

2013	Queensland	Drafted a <u>POLICY</u> for the management of fire fighting foam
2013	Dupont	Dupont make a statement it does not make, buy or use PFOA
2014	USEPA	<u>ADDED</u> new restrictions on long-chain perfluoroalkyl carboxylate (LCPFAC) chemical substances, and perfluorooctanoic acid (PFOA) or its salts.
2014	Helsingor Madrid	Statements made by group of scientists on the issue of PFC and advocating their disuse for PBT and CMR reasons affecting future generation
2014	NICNAS	Australia signatory to the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (the Convention) 10 May 2013

2014	Norway Germany	<u>SUBMISSION</u> to ECHA that PFOA and its salts and substances that degrade to PFOA (long chain PFC) in concentration greater equal to or greater than 2 ppb, shall not be manufactured, used or placed on the market as substances on their own, as constituents of other substances, in a mixture or in articles.
2015	CRC Care	Project to recommend screening values for sites contaminated by PFOS and PFOA, and its remediation and treatment
31 December 2015	USEPA	US EPA PFOA Stewardship Program ends
May 2016	Canada	<u>REGULATED</u> to prohibit the manufacture, import, use, sale and offer for sale of PFOA, its salts and its precursors and LC-PFCAs will come into force

PFOS Health Guidelines

PFOS	Drink water $\mu\text{g/L}$ (ppb)	Soil (resident) mg/kg (ppm)
Australia	None yet	None yet
Germany	0.1	
USEPA	0.2	6
Minnesota Department Health	0.3	
Minnesota Pollution Control Agency		2.1
Norway SFT		0.1
Canada	0.3	
UK	>0.3	
Dutch National Institute for Public Health and the Environment	0.65 ng/L (ppt) fresh water	

PFOA Health Guidelines

PFOA	Drink water $\mu\text{g/L}$ (ppb)	Soil (resident) mg/kg (ppm)
Australia	None yet	None yet
New Jersey US	0.04	
Germany	0.1	
Minnesota Department Health	0.3	
Minnesota Pollution Control Agency		2.1
Canada	0.3	
USEPA	0.4	16
West Virginia	0.5	
North Carolina	0.63	
UK	>0.3	

PFC Analysis Expectation

- PFOS
- PFOA
- 6:2 FTS (Fluorotelomers)
- 8:2 FTS (Fluorotelomers)
- PFHxA (Perfluorohexanoic acid)
- PFHxS (Perfluorohexane sulphonate)
- PFBS (Perfluorobutanoate)
- PFBA (Perfluorobutane sulphonate)

Interim Measure – Qld foam policy

- Whilst awaiting CRC Care project for screening values for PFOS and PFOA consider Qld foam policy Table 6.3.2 for contaminated water values
 - PFOS 0.3 µg/L (ppb)
 - PFOA 0.3 µg/L (ppb)
 - Perfluorinated carbon chain length 6 carbon atoms or smaller 0.3 µg/L (ppb)

Other Regulatory issues to consider

- Landfill and waste disposal acceptance criteria
- Transport of materials contaminated with PFOS, PFOA and fluorotelomers
- Premises treatment place licence conditions e.g. waste water treatment plant
- Thermal desorption and incineration licence conditions

Unfinished Business

- Short chain PFC (C3 to C6)
 - Perfluorobutanesulfonate (PFBS) – USEPA and MDH has position
 - Perfluoroethanesulfonate (PFES) and perfluoropropanesulfonate (PFPrS) now found more and more
- Fluorotelomers environment and health impact, and screening values in particular for long chain
- Definitive PFC guidance values for environment and health

Take Home Message

1. PFOS PFOA PBT and CMR issue
2. PFOS PFOA end point
3. PFC precursors degradation to PFOS and PFOA
4. PFOS and PFOA severely restricted or ban
5. Several drinking and soil guidance values – Australian none yet
6. Long chain fluorotelomers environmental and health issue
7. Short chain fluorotelomers deem to be environmentally friendly at this point in time but are still persistent in the environment
8. 6:2 FTS purity issue ie PFOA
9. No guidance values yet for fluorotelomers
10. PFC analytical validity and accuracy depends on sample preparation, standards and separation/detection technique and method
11. More and more research showing human health impacts of PFC homologues beside PFOS PFOA
12. Watch this space – New Bad Kid on the Block



FC (whether per or
poly) is still a cat,
and cat eats mice
and wildlife

Thank you

Questions and comments